Diffusion Kinetics in Radiation Chemistry. I. Generalized Formulation and Criticism of Diffusion Model

ARON KUPPERMANN AND GENEVA G. BELFORD
*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois**
(Received November 30, 1959)†

A generalized formulation of the diffusion-kinetic model of track effects in radiation chemistry is presented and criticized. It permits consideration of complex mechanisms, arbitrary initial distributions and radical correlation effects. Methods for the numerical integration of the associated differential equations on high-speed electronic digital computers are given and their accuracy is examined. Several applications are suggested.

1. INTRODUCTION

SOME important views that are presently accepted concerning the mechanism of the chemical effects of high-energy radiations (x rays, γ rays, and high-speed material corpuscles such as electrons, protons, α particles, fission products, etc.) are essentially the following ones.[1,2] Absorption of energy from these radiations by matter produces a variety of excited species, such as electronically excited molecules and ions in their ground or electronically excited states. Insofar as the absorption phenomenon is, in general, a highly localized one,[3] these species have a highly inhomogeneous spacial distribution and constitute the "tracks" of these radiations. The excited species are energetically unstable and undergo a sequence of transformations which terminate when thermodynamic equilibrium is reestablished. The first set of transformations in the direction of this equilibrium produces the attainment of thermal equilibrium but not of chemical equilibrium. The products of these transformations are stable molecules, some of which differ from those originally present, and chemically unstable species, such as free radicals. The next set of transformations consists of diffusion and chemical reactions involving these reactive species and produces, in the end, chemical equilibrium.

In systems such as dilute aqueous solutions, the relative amounts of the final products of the radiation-chemical reactions depend strongly on the degree of inhomogeneity of the spacial distributions of species in the tracks; dependences of this type are in general called "track effects." A diffusion-kinetic model for quantitatively explaining these effects was first clearly formulated and attacked by Lea.[4,5] After a few years of dormancy, it was modified by Samuel and Magee,[6] who were able to explain semiquantitatively the variation of primary radical and molecular yields in water with the LET (linear energy transfer) of the radiation used. Since then, this model has been able to provide a semi-quantitative explanation of the effect of scavenger concentration on those yields.[7–9]

In the Lea and Samuel-Magee models, several mathematical approximations were introduced to make the problem tractable analytically. The purpose of the series of papers, of which this is the first, is to describe the use of numerical methods to eliminate these approximations and, therefore, to submit the model to a more stringent test. The model is extended to include radical correlation and more complete kinetic schemes than those heretofore considered. Some points that will be analyzed in the calculations thus made possible are: the validity of the "prescribed diffusion" hypothesis[6–9]; the effect of solute diffusion on the calculated yields; the effect of the details of the shape and size of the initial radical distributions on the calculated yields; a possible explanation of the experimentally observed isotope effect; and the effect of secondary track reactions on the calculated yields. It is hoped that these calculations will show which features of the diffusion-kinetic model are consistent and which are inconsistent with the known experimental facts, as well as what modifications of the model should be introduced to decrease its inconsistencies.

In this paper, a general mathematical formulation of the diffusion-kinetic model is given in terms of a system of simultaneous, nonlinear, partial differential

* Work partially supported by the Atomic Energy Commission. Presented in part at the 136th Meeting of the American Chemical Society in Atlantic City, September, 1959.

† At the referee's suggestion, publication of this paper was postponed until the second one, which follows, was ready.

[1] R. L. Platzman, "The physical and chemical basis of mechanisms in radiation biology," in *Radiation Biology and Medicine*, edited by W. D. Claus (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), pp. 15–72; see also back references.

[2] Aron Kuppermann (a) J. Chem. Ed. **36,** 279 (1959); (b) "Diffusion kinetics in radiation chemistry," in *Actions Chimiques et Biologiques des Radiations*, edited by M. Haissinsky (Masson et Cie, Paris, 1961), 5th series, pp. 85–166; see also back references.

[3] Recent work by U. Fano [Phys. Rev. **103,** 1202 (1956); **118,** 451 (1960)] suggests that at least part of the absorption mechanism is a nonlocalized one. However, this does not preclude a relocalization of the energy at the time chemistry starts to occur. The possible effect of a homogeneous component in the initial distribution of radicals is mentioned in Sec. 2.5 and considered in a later paper of this series.

[4] D. E. Lea, *Actions of Radiations on Living Cells* (Cambridge University Press, Cambridge, England, 1946).

[5] D. E. Lea, Brit. J. Radiol., Suppl. **1,** 59 (1947).

[6] A. H. Samuel and J. L. Magee, J. Chem. Phys. **21,** 1080 (1953).

[7] J. L. Magee, J. chim. phys. **52,** 528 (1955).

[8] H. A. Schwarz, J. Am. Chem. Soc. **77,** 4960 (1955).

[9] H. Fricke, Ann. N. Y. Acad. Sci. **59,** 567 (1955).

equations. The physical foundations of the model are considered and criticized. The method used for preparing a general program for numerical integration of this system of equations on Illiac (the high-speed electronic digital computer of the University of Illinois) and the accuracy of the method are described. The initial conditions permitted in this program correspond to spherical spurs and cylindrical tracks with no variations along their axes.

In subsequent papers of this series, the results of the applications of this general program to particular models will be presented.

2. MATHEMATICAL FORMULATION OF GENERAL DIFFUSION-KINETIC MODEL

The over-all process of producing chemical transformations by the use of high-energy radiation starts with the bombardment of a material system by the radiation and terminates with the reestablishment of thermodynamic equilibrium. This process can be conveniently divided into three stages[1,2]:

(a) *Physical stage*, consisting of the dissipation of radiant energy in the system. Its duration is of the order of 10^{-13} sec or less.[10]

(b) *Physiochemical stage*, consisting of the processes which lead to the establishment of thermal equilibrium in the system. Its duration is usually of the order of 10^{-11} sec.

(c) *Chemical stage*, consisting of diffusion and chemical reaction of the reactive species, and leading to the establishment of chemical equilibrium. Its duration ranges from 10^{-8} sec upwards.

In the generalized diffusion-kinetic model it is assumed that by the beginning of the chemical stage certain chemically reactive "primary" species have been formed and are in thermal equilibrium with the surrounding medium. These species present a specific spatial distribution which depends on the quality of the radiation used. They then proceed to diffuse according to macroscopic diffusion laws and to react with themselves or with species already existing in the medium prior to irradiation. The products of these reactions may be chemically unstable and participate in further reactions, some of which may involve the "primary" reactive species. The rate laws obeyed by these reactions are assumed to be similar to those that would be obeyed if all the reactive species were distributed homogeneously, except that the rate constants for reactions among primary species are permitted to be time dependent in order to allow for correlation between particles of primary species.

The designation "primary" for the reactive species existing at the beginning of the chemical stage and produced as a consequence of the passage of high-energy radiation through the medium is really inappropriate, since they are themselves the result of a complex sequence of events involving species present prior to them. However, for simplicity of language, this term will be used in this and in future papers of this series. Also, the equations will be formulated only for gaseous and liquid media, since they are to be applied mainly to problems involving dilute aqueous solutions.

2.1 Categories of Species Considered in the Diffusion-Kinetic Model

Four categories of species will be considered. Three refer to reactive species and the fourth to nonreactive species. The first category comprises the several reactive species already present in the system before it is irradiated. These may include molecules of solvent and of one or more solutes contained in the system. They can react only with species from other categories. The second category contains the primary reactive species produced by the irradiation. The third category includes the secondary reactive species formed as a consequence of reactions involving the primary ones. The reaction leading from a primary to a secondary reactive species can be elementary, but can also be a sequence of elementary steps. For example, in the radiolysis of air-saturated dilute ferrous sulfate aqueous solutions, H or perhaps $e^-\cdot H_2O$ or $e^-\cdot aq$[11] is a primary species in the sense defined above; HO_2, which results from the reaction between primary H or $e^-\cdot H_2O$ or $e^-\cdot aq$ and solute (or "scavenger") O_2, is a secondary species; and Fe^{3+}, which results in part from the reaction between HO_2 and Fe^{2+} is also a secondary species, formed from H (or $e^-\cdot H_2O$ or $e^-\cdot$aq) in a reaction involving two elementary steps. Finally, the fourth category includes all products of the radiation-chemical reactions which are not reactive with any species ever present in the system during the chemical stage.

Let, in general, X_i represent any kind of species, be it reactive (primary, secondary, reactive solute or solvent) or not. These different kinds of species are differentiated from each other by the following notation:

For $i=1, 2, \cdots, p$

X_i denotes a reactive primary species.

For $i=p+1, \cdots, p+s$

X_i denotes a reactive secondary species.

For $i=p+s+1, \cdots, p+s+u=n$

X_i denotes a reactive solute (scavenger) or the solvent (if it is reactive).

[10] H. A. Dewhurst, A. H. Samuel, and J. L. Magee, Radiation Research **1**, 73 (1954).

[11] Evidence of more than one kind of species having chemical properties similar to those of H atoms has been recently reported: N. F. Barr and A. O. Allen, J. Phys. Chem. **63**, 928 (1959); G. Czapski, Summary of Proceedings of the Fourth Informal Conference on the Radiation Chemistry of Water, University of Notre Dame, March, 1961; F. S. Dainton (private communication).

For $i=n+1, \cdots, n+l$

X_i denotes a nonreactive species not initially present.

According to this notation, there are n $(=p+s+u)$ different reactive species, p of which belong to the category of reactive primary species, s to the category of reactive secondary species, and u to the category of reactive species already present prior to irradiation. Finally, there are l nonreactive species.

2.2 Diffusion and Reaction-Rate Laws in Terms of Probability Densities

Macroscopically, diffusion and reaction-rate laws are usually expressed in terms of concentrations (or activities) of the species involved. These concentrations are actually statistical averages of number densities. Such an average is conceptually obtained by considering a portion of the medium which contains a sufficiently large number of particles of each type so that statistical fluctuations are negligible. However, this portion should be sufficiently small so that by subdividing it into even smaller ones, the differences in number densities between any two must not be larger than would be expected on the basis of statistical fluctuations; i.e., there should be no detectable difference in the intensive properties of the smaller portions. Let us consider a particular example. We assume that a fluctuation of 1 part in 10^4 is negligible. Then, since the absolute fluctuation of the number of particles in a certain region of the medium is of the order of magnitude of the square root of that number,[12] an adequate portion of the medium that would be necessary to define a concentration of those particles should contain about 10^8 of them. If concentrations in the range 10^2 to 10^{-6} molar are considered, this adequate portion has a volume ranging from 10^9 to 10^{17} A^3. However, in track effects in the radiation chemistry of water, large changes in the number densities of radicals occur within volumes of the order of 10^3 to 10^6 A^3,[4-6] so that the concept of a radical concentration becomes meaningless. For this reason, probability densities must be used instead. Since each experimental observation includes a very large number of spurs or tracks—a typical example would be 10^{14} spherical spurs or 10^{10} cylindrical tracks—calculations based on probability densities should be able to predict accurately experimental results, if the theoretical model is a good one. In other words, each spur or track may have a relatively small number of reactive primary species, so that large statistical fluctuations can occur from spur to spur or track to track; however, the number of such spurs or tracks in any one experiment is sufficiently large so that statistical fluctuations in the final chemical measurements are negligibly small.

Let 0 be an arbitrarily chosen origin of coordinates. Let $c_i(\mathbf{r}, t)$ be, by definition, the probability density of finding a particle of species $X_i (i=1, 2, \cdots, n+l)$ at a position in the system determined by vector $\mathbf{r}$, at time t after the onset of the chemical stage. In other words, if we consider an infinite ensemble of replicas of the system, $c_i(\mathbf{r}, t)$ would be the average number density of particles of kind X_i at position $\mathbf{r}$ and instant t. For systems in which the definition of concentration is meaningful (according to the conditions given in the preceding paragraph), the probability density c_i is equal to the concentration. Consequently, c_i can be thought of as a generalized concentration, valid even when very small numbers of particles are considered or when very steep concentration gradients are involved.

It is of interest to consider the normalization properties of the probability densities $c_i(\mathbf{r}, t)$ defined above. Let

$$N_i(t) = \int c_i(\mathbf{r}, t)\, d\mathbf{r}, \tag{1}$$

where the integral is extended over the total volume of the system. If X_i is a primary or secondary species, or a nonreactive species not initially present, then $N_i(t)$ is the average number of particles of species X_i present in the system at time t. For secondary species, as well as nonreactive species not initially present, $N_i(t)$ vanishes at $t=0$. If the system is infinite, then $N_i(t)$ would be infinite for solutes homogeneously distributed at time zero or for the solvent; this makes it convenient not to define $N_i(t)$ for this category of species.

It is assumed that the diffusion and reaction-rate laws that hold for systems in which the usual concept of concentration is meaningful continue to be valid for systems of the type found in radiation chemistry, with probability densities substituting for concentrations whenever they appear, and rate constants being time-dependent to allow for particle correlation. The physical basis for this assumption will be discussed in Sec. 3.

2.3 Generalized Reaction Mechanism

It will be assumed that any kind of species can disappear or be formed by any first or second order reaction occurring in the bulk of the system. These reac-

[12] This follows from the general statistical result that the *relative* fluctuation of any additive property of a macroscopic system is inversely proportional to the square root of the number of particles in that system. See, for example, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1958), p. 8.

tions can thus be generally represented by

$$X_i \xrightarrow{k_i} \text{Products} \qquad \text{1st-order disappearance} \qquad [1]$$

$$X_i + X_j \xrightarrow{k_{ij}} \text{Products} \qquad j=1, 2, \cdots, n \qquad \text{2nd-order disappearance} \qquad [2]$$

$$X_a \xrightarrow{k_{a_i}} X_i + \text{Products} \qquad a=1, 2, \cdots, n \qquad a \neq i \qquad \text{1st-order appearance} \qquad [3]$$

$$X_b + X_d \xrightarrow{k_{b_i d_i}} X_i + \text{Products} \qquad b, d=1, 2, \cdots, n \qquad b, d \neq i \qquad \text{2nd-order appearance.} \qquad [4]$$

All rate constants above refer to the rate of disappearance of reactants and are permitted to be time dependent. If X_i is a nonreactive species, k_i and k_{ij} vanish.[13] The purpose of introducing first-order reactions is to permit simple inclusion of reactions involving the solvent and to simplify the diffusion kinetic equations when a scavenger can be considered to diffuse infinitely fast.

2.4 Diffusion-Kinetic Equations

The chemical effects of the bombardment of a system by a stream of high energy particles or electromagnetic quanta can, for dose-rates that are not too high (i.e., for sufficiently low space-time densities of absorbed energy), be pictured as a sum of the separate effects of individual quanta or particles. In this case, the extent of chemical effects depends on the total dose (i.e., total energy absorbed by the system) but not on the dose rate. It is for these conditions of lack of dose-rate effects that the equations will be formulated. Dose-rate effects have been included by Magee[7] in an approximate one-radical model.

In the absence of dose-rate effects, it is sufficient to consider the effect of the absorption of energy from a single incident high-energy quantum or particle. The total result is obviously obtained by multiplying the one-particle effect by the number of quanta or particles whose energy was absorbed. Furthermore, it is assumed that, at the beginning of the chemical stage, the absorption of energy from a single quantum or particle has brought about a certain initial distribution of primary reactive species which is in thermal equilibrium with the medium. These species are assumed to diffuse and react, but not to interact with species formed by other quanta or particles. (The order of magnitude of the does rates for which this happens has been calculated by Lea.[4]) Under these assumptions, the time rate of change of the probability density of X_i at a fixed position $\mathbf{r}$ of the medium is the algebraic sum of the effects of the net rate of diffusion of particles X_i to this position and their rates of appearance and disappearance due to reactions occurring at this position. Consequently, for the general mechanism described in Sec. 2.3, and the laws assumed at the end of Sec. 2.2, one can write

$$\partial c_i(\mathbf{r}, t)/\partial t = D_i \nabla^2 c_i - k_i c_i - \sum_{j=1}^{n} k_{ij} c_i c_j + \sum_{a=1}^{n}{}' k_{a_i} c_a$$

$$+ \sum_{b,d=1}^{n}{}' (1-\tfrac{1}{2}\delta_{bd}) k_{b_i d_i} c_b c_d \qquad i=1, 2, \cdots, n. \qquad (2)$$

All symbols in Eqs. (2) have been defined, except D_i, which is the diffusion coefficient of X_i; δ_{ij}, which is the usual Kronecker symbol ($=1$ for $i=j$ and 0 for $i \neq j$), and ∇^2, which is the usual three-dimensional Laplacian operator. The reason for the parenthesis containing the Kroenecker δ is that when $b=d$, the reaction

$$X_b + X_d \rightarrow X_i + \text{products}$$

becomes

$$2X_b \rightarrow X_i + \text{products}$$

and the rate of appearance of X_i is one-half the rate of disappearance of X_b. Since the latter is given by $k_{b_i b_i} c_b^2$, the former is given by $\frac{1}{2} k_{b_i b_i} c_b^2$. The primes in the last two summation signs in Eqs. (2) mean that in them none of the quantities a, b, d can assume the value i.

Equation (2) constitutes a set of n simultaneous nonlinear partial differential equations which, in general, can not be integrated analytically. These equations involve only the reactive species. The amounts of nonreactive species formed can be calculated from the c_i of the reactive species, as described in Sec. 2.6.

[13] It should be observed that according to this notation there exists a subtle difference between $k_{b_i d_i}$ and k_{bd}. The quantity k_{bd} refers to the rate constant of a reaction between X_b and X_d, whereas $k_{b_i d_i}$ refers to a reaction between X_b and X_d in which, in addition, X_i is a product. Consider, for example, the case in which the only primary species is X_1, the only secondary species are X_2 and X_3 and the only reactive solute is X_4, the solvent and all other species being unreactive. Let the reaction mechanism be

$$2X_1 \rightarrow X_2,$$

$$X_2 + X_4 \rightarrow X_3 + X_5,$$

$$X_1 + X_3 \rightarrow X_6.$$

In this case, although $k_{11} \neq 0$, i.e., X_1 reacts with itself, $k_{1_3 1_2} = 0$, i.e., X_3 is not a product of that reaction. The only nonvanishing $k_{a_2 b_2}$ is $k_{2_3 4_2} = k_{24}$. A similar observation holds for the difference between k_{a_i} and k_a.

2.5 Initial Distributions and Boundary Conditions

Historically, the first theory of diffusion kinetics was applied by Jaffe[14,15] to explain the ionization currents obtained in gases and liquids irradiated by ionizing radiation, with and without the presence of a collecting electric field. His basic model was that the ions formed were distributed in axially homogeneous cylindrical tracks. He assumed that the initial distribution of the ions, in planes perpendicular to the axis of cylinder, was a Gaussian function of the distance to the axis. The ions then proceeded to neutralize each other by recombination in the track or to diffuse away from it and eventually be collected giving rise to the ionization current. The essential difference between the different kinds of radiation was considered to be the density of ions along the cylindrical track. He obtained good agreement between theory and available experimental data for the amount of ion-ion recombination within a track for gases irradiated by α rays at atmospheric pressure and high pressure. Later Lea[16,17] criticized the application of this model to β and γ ray induced ionization and greatly improved the agreement between theory and experiment, for gases at about 100 atm irradiated by these radiations, by substituting the cylindrical ion-track by a string of spherically symmetrical ion-clusters. Lea also used an initial distribution of ions that was Gaussian with respect to the distance to the axis of the cylindrical track or center of the spherical cluster. He justified this initial distribution[17] on physical grounds by considering the mean displacement of an electron as it moves away from the parent ion, before it becomes attached to a neutral molecule.

The application of these ideas to explain the effect of radiation quality on the chemical reaction induced in water and dilute aqueous solutions by high-energy radiation was first done by Lea.[4,5] He adopted the point of view suggested by others that the chemical effects observed could be accounted for by assuming the formation of H and OH radicals. He then postulated a certain mechanism of formation of these radicals. According to this, the H and OH radicals formed by the decomposition of excited neutral water molecules was ignored because they would probably recombine very rapidly due to their small initial separation (this has been since shown to be incorrect: The quantum yield for available radical pairs in water irradiated by light of about 1900 A is roughly $\frac{1}{2}$.[18]) The OH formed from H_2O^+ would result from a very rapid dissociation of this ion, and be located very close to the position at which ionization occurred. The electron liberated in the act of ionization would have an energy of a few electron volts and would travel a distance of many tens of Angstroms before becoming attached either to a hydrogen ion or a water molecule. In either case a hydrogen atom would be formed at the site of attachment, quite far away from the hydroxyl radical, so that no immediate recombination of the two would occur. This mechanism of H formation would produce an initial distribution of this species equal to the initial distribution of negative ions. Lea assumed that for all kinds of high-energy radiation, the spherical ion clusters along the incident charged particle or secondary fast electron were sufficiently close together for a cylindrical track to be formed before any appreciable recombination took place. Accordingly, the initial distribution of H atoms was taken to be an axially homogeneous cylinder, with a Gaussian distribution in a plane perpendicular to the axis of the cylinder (as justified theoretically for negative ions).[17] The radius of this Gaussian distribution (measured, for example, by the average distance of the H atoms to the axis of the cylinder) was inferred to be of the order of 150 A from Wilson chamber experiments[19] with x rays in gases. Lea also arbitrarily assumed that the OH had an initial cylindrical Gaussian distribution around the axis of the α particle or fast electron track, with a radius of the order of 20 A.

Lea's model was modified in 1953 by Samuel and Magee,[6] who postulated a different mechanism for the formation of H and OH radicals and, as a consequence, different initial distributions. According to them, it is probable that after a time interval of the order of 10^{-13} sec after the passage of the ionizing radiation, slow electrons produced as a result of the ionization of water molecules are recaptured by the parent ion forming an excited water molecule which may lose energy by dissociation into radicals. According to this picture, a spur (or "cluster" in the nomenclature of references 16 and 17) in liquid water would consist of an equal number of H and OH radicals and would have a radius of the order of 10 A (rather than the 150 A radius for the H distribution assumed by Lea).[4,5] As a result, in the case of fast electrons (including the secondary electrons produced by γ rays or x rays), these spurs would be sufficiently far apart so that by the time they expanded sufficiently to interact, all reactions were over. Thus, Samuel and Magee treated the radiation chemistry of fast electrons in liquid water in a manner similar to Lea's treatment[16,17] of these electrons in the recombination of ions in gases at high pressures. They also assumed, both in the case of isolated spherical spurs or long cylindrical tracks, Gaussian initial distributions. This assumption was prompted by mathematical expediency; the theoretical justification of the Gaussian distribution of negative ions used by Lea does not

[14] G. Jaffe, Ann. Physik, Ser. 4 **42**, 303 (1913).
[15] G. Jaffe, Physik. Z. **30**, 849 (1929).
[16] D. E. Lea, Proc. Cambridge Phil. Soc. **30**, 80 (1934).
[17] E. Kara-Michailova and D. E. Lea, Proc. Cambridge Phil. Soc. **36**, 101 (1940).
[18] J. L. Weeks and M. S. Matheson, *Proceedings of the Second International United Nations Conference on the Peaceful Uses of Atomic Energy* (United Nations, Geneva, 1958), Vol. 29, pp. 385–390.
[19] O. Klemperer, Z. Physik **45**, 225 (1927).

have any bearing on the distribution of radicals formed by a Magee-Samuel mechanism.

The basic view of both Lea and Magee is then that the track of an energetic charged particle, be it the incident particle as in the case of an α particle, or a secondary electron, as in the case of x or γ rays, is formed of a string of spherically symmetrical spurs of free radicals, distributed in a Gaussian manner around the center. Two extreme cases are recognized: one in which the spurs are initially so far apart that no interaction between radicals of neighboring spurs can occur, and the other in which the spurs are so close together from the very beginning that they effectively merge into a cylindrical track. The main difference between these two authors is that Lea considers both the α-particle case and the γ- or x-ray case to belong to the second extreme, whereas Magee considers the α-particle case in a similar manner, but assumes that the γ- and x-ray cases belong to the first extreme case, i.e., the spurs along a track are so far apart that they do not interact. This latter view has been very successful in explaining in a semiquantitative manner the difference between the yields in γ rays and α particles.[6]

The choice of an initial distribution of primary reactive species includes then two choices in reality. One of them involves the distribution of primary species within a spherical spur; the other refers to the distribution of spherical spurs along the track of a charged particle.

In considering the distribution of primary species within a spherical spur, all papers dealing with track effects in radiation chemistry have adhered to the arbitrary assumption of initial Gaussian distributions,[4–9,20–25] partially owing to mathematical expediency in analytical treatments. However, as Platzman pointed out,[1] the form of the initial distribution may be expected to have a significant effect on the solutions of the diffusion-kinetic equations. For these reasons, it was decided to permit these distributions to remain arbitrary in this model and to investigate the effects of different kinds of initial distributions on the calculated relative yields. One of these could include distributions having a spacially homogeneous component, suggested by the recent work mentioned in the footnote 3.

When considering the distribution of spherical spurs along the track of a charged particle, one must examine cases of low, intermediate, and high LET.

For sufficiently low LET and in the presence of reasonably efficient scavengers, the spurs are sufficiently separated so that they do not interact with each other; by the time neighboring spurs expand sufficiently to interact, all primary species have entirely disappeared by reaction. For this situation, and that of low dose rates, the medium can be considered to be infinite, since under ordinary experimental conditions it is many orders of magnitude larger than the volume of a spur, even after the latter has had time to expand by diffusion. The diffusion-kinetic equations (2) then have spherical symmetry and contain a single space coordinate, namely, the distance r to the center of the spur. To compare calculations based on these assumptions with experiment, it is further necessary to consider a distribution function for the initial numbers of primary species per spur.[6]

For intermediate values of the LET, the spherical spurs interact. A reasonable approximation is to assume that spurs that are sufficiently close to interact lie on a straight line. Since, in general, the energy of the charged particles is of the order of 10^4 ev or more, and the energy dissipation per spur is of the order of magnitude of 100 ev,[6] there are many spurs per track. Therefore, track-end effects, which involve only a few spurs, may be neglected. In describing a string of spurs of this type, an important parameter is the average distance between neighboring spurs. This quantity depends on the linear rate of energy dissipation at the position on the track that is being considered. This rate increases along the track as the particle slows down. Since, however, it does not change very much over the distance of a few spurs, and since spurs farther away from each other than that do not interact,[26] it is possible to restrict the calculations to tracks along which the rate of energy dissipation by the particle does not change. To compare these calculations with experimental results, it is necessary, however, to use an adequate distribution of these constant-rate-of-energy dissipation tracks to take into account the fact that in actual tracks this rate continuously varies. An additional consideration in tracks of intermediate LET values is that the distribution of the distance between neighboring spurs should be random[21]; subject, of course, to the restriction of having the correct average value mentioned above. For low dose rates (no interaction between tracks) and linear strings of spurs, the number of space coordinates necessary to describe the problem is two: a distance along the axis of the track and a distance to the axis of the track. Cylindrical symmetry about the linear axis makes it unnecessary to use a third space coordinate.

For sufficiently high values of the LET the spherical spurs are sufficiently close together so that, over a distance of many spurs, the track becomes a cylinder

[20] J. L. Magee, J. Am. Chem. Soc. **73,** 3270 (1951).
[21] A. K. Ganguly and J. L. Magee, J. Chem. Phys. **25,** 129 (1956).
[22] L. Monchick, J. L. Magee, and A. H. Samuel, J. Chem. Phys. **26,** 935 (1957).
[23] D. A. Flanders and Hugo Fricke, J. Chem. Phys. **28,** 1126 (1958); Hugo Fricke and D. L. Phillips, *ibid.* **32,** 1183 (1960); **34,** 905 (1961).
[24] P. J. Dyne and J. M. Kennedy, Can. J. Chem. **36,** 1518 (1958); **38,** 61 (1960).
[25] V. Yu. Filinovskii and Yu. A. Chizmadzhev, Proceedings of the First All-Union Conference on Radiation Chemistry, Akad. Nauk S.S.S.R., Moscow, 1958, p. 19.

[26] A. Kuppermann and G. Belford, J. Chem. Phys. **36,** 1427 (1962), following paper; also, subsequent papers in this series.

with practically no variations in the initial probability density of primary species along the axis of the track, which means that for calculation purposes it may be considered to be infinitely long. Actually, as the particle loses energy along the track, this density increases, goes through a maximum, and finally drops to zero. However, in a first approximation and for reasons similar to those given in the preceding paragraph, calculations can be restricted to tracks in which this variation is neglected.[27] For comparison with experiment, adequate distributions of the rate of energy dissipation must be considered. Since, as in the case of isolated spherical spurs, the medium can be considered to be infinite for conditions under which no dose-rate effects occur (no interaction between tracks), the diffusion-kinetic Eqs. (2) for axially homogeneous cylindrical tracks have homogeneous cylindrical symmetry around the axis of the track. Hence, the problem can once more be described by a single space coordinate, namely the distance to the axis of the track.

Finally, there might arise situations in which the most appropriate initial condition presents neither spherical nor cylindrical symmetry. In these cases, all three space dimensions are necessary to describe the problem, so that there are a total of four independent variables in Eqs. (2). This increases the computational time required for numerical integration of these equations, but does not change any other important characteristic of it. Last, but not least, it must be remembered that as ionizing radiation traverses the medium, it produces secondary, tertiary, etc., electrons of varying energies,[28–31] so that one must consider, in the initial distribution, this complex spectrum of energy dissipation. However, one can divide up the several tracks involved into groups of high, intermediate, and low LET and cope with these simpler initial distributions as described above. As a final step, it is necessary to add up the effects of these several tracks. This could be described as a kind of "averaging" over the LET distribution characteristic of the radiation considered. Great care, however, must be taken in carrying out this process. For instance, tracks of soft secondary electrons of short range can be considered cylindrical, but end effects may not be negligible. Therefore, the contribution from such electrons might be different from, let us say, that of α particles of the same LET.

Regardless of the details of the initial distribution, some secondary species may be formed which are relatively unreactive; i.e., which participate in reactions whose rates are small compared to rates of primary species reactions or of diffusion. These slow reactions may occur, to a large extent, homogeneously, and do not produce any "track effects." They can be easily taken into account as indicated in a particular case in Sec. 2.8. The word "interaction" in the previous three paragraphs refers to species undergoing reactions whose rate is comparable to the rate of diffusion.

The initial conditions for nonprimary species are obvious: $c_i(\mathbf{r}, 0) = 0$ for secondary species and $c_i(\mathbf{r}, 0) =$ initial concentration for homogeneous solvents and solute.

The boundary conditions for all cases fix the values of the c_i at *infinite values of the space coordinates* and at *any instant of time.* For each primary and secondary species, this probability density is zero, whereas for solution or solvent distributed homogeneously at time zero, it is equal to its initial value.

2.6 Quantities to be Compared with Experiment

The experimental quantities of radiation chemistry are the so-called G values. Let X_j be any product present in the system after the radiation chemical reactions are over. Then, by definition, $G(X_j)$ is the number of X_j particles (molecules, ions, etc.) formed per 100 ev energy absorbed by the irradiated medium. Although the units of $G(X_j)$ are molecules/100 ev, they are usually omitted. In order to be able to calculate G values from Eqs. (2), it would be necessary to include, among the initial parameters, the amount of energy necessary to form a primary species, in addition to the diffusion coefficients, rate constants and initial conditions. This information is not usually available, so that approximate estimates would have to be made. These estimates can be avoided, and the energy absorbed per spur or track can be eliminated from the picture, by calculating ratios of G values and comparing these with the experimental ratios. Another aspect of the problem of the *a priori* calculation of correct absolute G values will be discussed in Sec. 3.

Ratios of G values may be calculated from solutions of Eqs. (2) in the following way. The average number of particles of species X_i formed during time interval 0 to t owing to each one of the reactions [1] through [4] is given respectively by the quantities

$$-M_i(t) = -\int_0^t d\theta \int_{\text{system}} k_i c_i(\mathbf{r}, \theta)\, d\mathbf{r}, \tag{3}$$

$$-M_{ij}(t) = -\int_0^t d\theta \int_{\text{system}} k_{ij} c_i(\mathbf{r}, \theta) c_j(\mathbf{r}, \theta)\, d\mathbf{r}, \tag{4}$$

$$M_{a_i}(t) = \int_0^t d\theta \int_{\text{system}} k_{a_i} c_a(\mathbf{r}, \theta)\, d\mathbf{r}, \tag{5}$$

$$(1-\tfrac{1}{2}\delta_{bd}) M_{b_i d_i}(t) = (1-\tfrac{1}{2}\delta_{bd}) \int_0^t d\theta \int_{\text{system}} k_{b_i d_i} c_b(\mathbf{r}, \theta) c_d(\mathbf{r}, \theta)\, d\mathbf{r}. \tag{6}$$

[27] Close to the end of the track of a densely ionizing particle, such as a Po^{210} α particle, the LET changes very rapidly with distance and a significant fraction of the initial energy of the particle is dissipated in this region. Adequate consideration of the effect of this phenomenon on the chemical yields might require the use of a model in which diffusion along (as well as away from) the axis of the track is included. This problem will be further considered in other papers of this series.

[28] L. H. Gray, J. chim. phys. **52,** 519 (1955).

[29] P. R. J. Burch, Brit. J. Radiol. **30,** 524 (1957).

[30] P. R. J. Burch, Radiation Research **6,** 289 (1957).

[31] P. R. J. Burch, Radiation Research **11,** 481 (1959).

The negative signs in Eqs. (3) and (4) are due to the fact that these equations correspond to reactions in which X_i is a reactant rather than a product. All the M's defined above are positive. The net average number of particles of X_i formed during time interval 0 to t and due to all reactions which occur in the chemical stage is then given by

$$F_i(t)=\sum_{a=1}^{n}{}'M_{a_i}(t)+\sum_{b,d=1}^{n}{}'(1-\tfrac{1}{2}\delta_{bd})M_{b_id_i}(t)-M_i(t)-\sum_{j=1}^{n}M_{ij}(t). \quad (7)$$

Equations (3) through (7) are valid for any of the $n+l$ species X_i, whether reactive or nonreactive. Nevertheless, all probability densities c which appear in them refer to one of the n reactive species. This makes it sufficient to solve the system of n Eqs. (2) involving only reactive species, rather than an equivalent system of $n+l$ equations involving both the reactive and unreactive species.

The net average number of particles of X_i formed during the entire chemical stage due to all reactions which occur during that stage is, therefore, $F_i(\infty)$. This average refers to the infinite statistical ensemble discussed in Sec. 2.2. Before a quantity which can be compared with experiment is obtained, further averaging over certain initial parameters (such as number of primary species per spur) mentioned in Sec. 2.5 must be performed. This averaging process furnishes a quantity $\bar{F}_i(\infty)$ which should be proportional to $G(X_i)$, the constant of proportionality being independent of i. Thus the relationship

$$\bar{F}_i(\infty)/\bar{F}_j(\infty)=G(X_i)/G(X_j) \quad (8)$$

should hold for any pair of species X_i and X_j present and measurable at the end of the chemical stage, if the model is adequate. This is the experimental test of the model. The parameters that determine the $\bar{F}_i(\infty)$ are the rate constants (and hence mechanism), diffusion coefficients and initial distribution parameters. The independent experimental variables are the quality of the radiation, the kinds of solutes and the concentrations of these solutes. Some of the diffusion coefficients (such as those of the solutes) and some of the rate constants can be measured experimentally. It is possible that in the future more and perhaps all parameters of this type will be determined by independent experiments. Then the number of unknown parameters of the model would be much smaller than the amount of experimental information, and this would permit the model to be put to a very stringent test. However, even in the absence of accurate knowledge of these parameters, some important features of the model can be tested against experiment, by using simplified forms of the model and "reasonable" values (order of magnitude estimates) of the unknown parameters. This point will be further developed in Sec. 3.

2.7 Conservation Relations

A conservation relation exists for each species X_i present in the system in finite amount (which excludes the solvent or solutes homogeneously distributed at $t=0$ in infinite systems). According to this relation, the average number $N_i(t)$ of particles of X_i present at time t, minus the net number formed in time interval 0 to t due to the chemical reactions equals the average number of the particles initially present:

$$N_i(t)-F_i(t)=N_i(0). \quad (9)$$

This expression permits a test of the accuracy of numerical methods for integrating Eqs. (2) (see Sec. 4.5). It can be easily seen that the solutions of these equations which satisfy the initial and boundary conditions mentioned in Sec. 2.5 will also satisfy Eq. (9). Indeed, integration of both sides of Eqs. (2) over the volume of the system followed by an integration over time between 0 and t will furnish Eqs. (9), since it follows from the theorem of the divergence[32] and the finiteness of N_i that the space integral of $\nabla^2 c_i$ vanishes. Actually Eq. (9) describes a well-established basic law of chemistry, and the diffusion-kinetic model was, of course, chosen so as to satisfy it.

In addition to the conservation relations represented by Eqs. (9), the conservation relations involving the constancy of the number of atoms of each element in chemical reactions furnish additional means of checking the accuracy of numerical procedures for integrating Eqs. (2).

2.8 A Particular Example

A relatively simple example is the radiation chemistry of dilute oxygen-free solutions of ferrous sulfate in 0.8 N sulfuric acid. A mechanism which has been postulated to explain the experimental facts is[33,34]

$$\mathrm{OH}+\mathrm{OH}\xrightarrow{k_5}\mathrm{H_2O_2}, \quad [5]$$

$$\mathrm{H}+\mathrm{H}\xrightarrow{k_6}\mathrm{H_2}, \quad [6]$$

$$\mathrm{OH}+\mathrm{Fe^{2+}}\xrightarrow{k_7}\mathrm{OH^-}+\mathrm{Fe^{3+}}, \quad [7]$$

$$\mathrm{H}+\mathrm{H^+}\xrightarrow{k_8}\mathrm{H_2^+}, \quad [8]$$

$$\mathrm{H_2O_2}+\mathrm{Fe^{2+}}\xrightarrow{k_9}\mathrm{Fe^{3+}}+\mathrm{OH}+\mathrm{OH^-}, \quad [9]$$

$$\mathrm{H_2^+}+\mathrm{Fe^{2+}}\xrightarrow{k_{10}}\mathrm{Fe^{3+}}+\mathrm{H_2}. \quad [10]$$

[32] See, for example, H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1943), p. 154.

[33] T. Rigg, G. Stein and J. Weiss, Proc. Roy. Soc. (London) **A211**, 375 (1952).

[34] W. G. Rothschild and A. O. Allen, Radiation Research **8**, 101 (1958).

The primary reactive species are OH and H, the secondary reactive species are H_2O_2 and H_2^+, the reactive solutes are Fe^{2+} and H^+ and the nonreactive species of interest are H_2 and Fe^{3+}. The diffusion-kinetic equations corresponding to reactions [5] through [10] are

$$\partial[OH]/\partial t = D_{OH}\nabla^2[OH] - k_5[OH]^2 - k_7[OH][Fe^{2+}] + k_9[H_2O_2][Fe^{2+}], \quad (10)$$

$$\partial[H]/\partial t = D_H\nabla^2[H] - k_6[H]^2 - k_8[H][H^+], \quad (11)$$

$$\partial[H_2O_2]/\partial t = D_{H_2O_2}\nabla^2[H_2O_2] - k_9[H_2O_2][Fe^{2+}] + \tfrac{1}{2}k_5[OH]^2, \quad (12)$$

$$\partial[H_2^+]/\partial t = D_{H_2}+\nabla^2[H_2^+] - k_{10}[H_2^+][Fe^{2+}] + k_8[H][H^+], \quad (13)$$

$$\partial[Fe^{2+}]/\partial t = D_{Fe^{2+}}\nabla^2[Fe^{2+}] - k_7[OH][Fe^{2+}] - k_9[H_2O_2][Fe^{2+}] - k_{10}[H_2^+][Fe^{2+}], \quad (14)$$

$$\partial[H^+]/\partial t = D_{H^+}\nabla^2[H^+] - k_8[H][H^+]. \quad (15)$$

The amounts of H_2 and Fe^{3+} formed are given by

$$F_{H_2}(\infty) = \int_0^\infty dt \int_{\text{system}} (\tfrac{1}{2}k_6[H]^2 + k_{10}[H_2^+][Fe^{2+}])\, d\mathbf{r}, \quad (16)$$

$$F_{Fe^{3+}}(\infty) = \int_0^\infty dt \int_{\text{system}} \{k_7[OH] + k_9[H_2O_2] + k_{10}[H_2^+]\} \times [Fe^{2+}]\, d\mathbf{r}. \quad (17)$$

For simplicity, $c_i(\mathbf{r}, t)$ was substituted by $[X_i]$ in Eqs. (10) through (17). Other obvious changes were made in the indexing of the D's, k's, and F's.

Actually, reaction [9] is much slower than the rest so that by the time all others are over there will still be some H_2O_2 present which will react homogeneously with Fe^{2+} in the bulk of the system. Effects such as these can easily be taken into account in the calculations. In this case, for example, to a very good approximation k_9 can be assumed to be zero, and Eq. (12) can be neglected. Then $F_{H_2}(\infty)$, $F_{Fe^{3+}}(\infty)$ and $F_{H_2O_2}(\infty)$ can be calculated. The quantity to compare with $G(Fe^{3+})$ would then be $F_{Fe^{3+}}(\infty)+2F_{H_2O_2}(\infty)$ since eventually each H_2O_2 molecule is responsible for the oxidation of two Fe^{2+} ions. This means that the only reactions of importance insofar as track effects are concerned are those which are sufficiently rapid for them to occur to an appreciable extent before the spurs or tracks from different particles merge.

3. CRITICISM AND PHYSICAL BASIS OF MODEL

The first assumption of the diffusion-kinetic model, given in Sec. 2, is that at the beginning of the chemical stage there exist "primary" reactive species in thermal equilibrium with the surrounding medium. These are assumed to be H (or perhaps $e^-\cdot H_2O$ or $e^-\cdot aq.$) and OH radicals in the case of water. As Platzman has pointed out,[1] this precludes the possibility of unconventional chemistry during the physico-chemical stage. Also, in some systems, the physico-chemical and chemical stages may overlap, energy transfer processes which do not lead to reaction occurring simultaneously and in competition with chemical reactions. The presence of scavengers, which influence the chemical processes, could also influence in a direct manner and according to nondiffusive type laws the energy transfer process. Under such circumstances, the diffusion-kinetic Eqs. (2) might be expected not to be applicable. These could be serious criticisms of the model; however, it is conceivable that the errors introduced by ignoring these effects could, for many systems, be quite small. This seems at present to be the case for water and dilute aqueous solutions.[2b]

The second assumption is that the diffusion of the primary and other species obey Fick's macroscopic diffusion laws.[35] This assumption has been shown by Smoluchowski[36] to describe correctly, in terms of probability densities, the relative Brownian motion of colloidal particles in a liquid medium, after a correction term involving particle interaction is included. Kirkwood[37,38] showed that the Smoluchowski equation is also applicable to the relative motion of molecules in a liquid, for observation times greater than about 10^{-13} sec.[39] Monchick[39] used the Smoluchowski equation to describe a system formed by a pair of particles capable of reacting with each other in a liquid containing a reactive solute. He applied this model to photodissociation in solution and was able to get good agreement between theory and experiment. The validity of macroscopic diffusion laws for microscopic systems seems to rest on a satisfactory statistical mechanical foundation.

A third assumption of the model is that the reaction-rate laws governing the reactions between particles in tracks are similar to those that would govern these reactions in a macroscopic homogeneous system, but with the rate constants being made time-dependent. Monchick *et al.*[22] have shown that, for rate constants that are time independent, the assumption of ordinary reaction-rate laws is equivalent to the neglect of correlation between the particles. This neglect is probably not justified in track effects. For example, it might be expected that, in the case of liquid water, an H and OH radical resulting from the dissociation of an excited water molecule would tend to recombine with each other more effectively than would be indicated by a rate constant measured in bulk homogeneous experiments. Monchick showed, however, that to some extent correlation could be introduced by assuming the

[35] A. Fick, Pogg. Ann. **94**, 59 (1855).
[36] M. v. Smoluchowski, Ann. Physik **48**, 1103 (1915); Z. physik. Chem. **92**, 129 (1917).
[37] J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946).
[38] J. G. Kirkwood, F. P. Buff, and M. S. Green, J. Chem. Phys. **17**, 988 (1949).
[39] L. Monchick, J. Chem. Phys. **24**, 381 (1956).

rate constants to decrease with time according to appropriate laws. Thus our third assumption also seems to be a reasonable one.

An apparently serious criticism of the model is that it contains so many parameters that it should always be possible to choose their values so as to fit experiment. On the other hand, as mentioned at the end of Sec. 2.6, these parameters are rate constants, diffusion coefficents, and initial distribution parameters. At least in principle, the rate constants and diffusion coefficients can be determined by independent experiments, so that these do not provide flexibility to the model in a permanent sense. For the time being, our ignorance of many of these quantities does perhaps allow some additional flexibility; this, however, should be recognized as an inadequacy of the present state of experimental knowledge about properties of radicals in solution rather than as a weak point of the model. The initial distribution parameters are also measurable in principle, but their direct determination presents technical problems which might take appreciable time to be solved. Nevertheless, the model can still be quite stringently tested if the other parameters are known, since the initial conditions depend only, for a given medium and physical conditions, on the radiation used, and are invariant with respect to other experimental variables such as the nature and concentration of solutes. Thus the number of experimental points to be explained could be much larger than the number of unknown parameters which characterize that initial distribution. In addition, another feature of the model is that certain of its properties are independent of the exact numerical values of some of the parameters, which, as a result, need not be precisely known to test the model. For example, let us consider the decrease of $G(H_2)$ and $G(H_2O_2)$ with scavenger concentration in aqueous solutions. Schwarz[8] has shown that if the ratios $G(H_2)/G_0(H_2)$ and $G(H_2O_2)/G_0(H_2O_2)$ are plotted against scavenger concentration for several scavengers (G_0 being the extrapolated yield corresponding to absence of scavenger) in the γ-ray radiolysis of dilute aqueous solutions, the several curves can be made to coincide by a horizontal translation of the systems of coordinates. To interpret this fact, Schwarz made a calculation for a one-radical one-scavenger model, using a Gaussian initial distribution, a "prescribed-diffusion" hypothesis, and assuming that the concentration of scavenger in the spurs did not change with position or time and that spurs of different initial number of radicals had *equal* radical densities (because of different initial radii). The theoretical curve thus obtained showed the same general shape as the experimental one, but had a different curvature, so that deviations from the experimental G ratios appreciably larger than the experimental error were found. Since then the equations corresponding to this model (see Sec. 5) have been integrated numerically,[2,23,26] without using the "prescribed diffusion" hypothesis and permitting the scavenger concentration to change with position and time, the other assumptions being maintained. The results agreed with Schwarz's. Regardless of the parameters chosen for the initial spherical Gaussian distribution or of the values of the time-independent rate constants and diffusion coefficients, agreement between theory and experiment could not be improved. Thus it can be stated that this one-radical, spherical, Gaussian model, which does not include a distribution function for the initial radical densities at the spur centers, is not an entirely adequate explanation of the experimental facts *regardless* of the values of the unknown parameters. The lack of knowledge of these parameters did not interfere with a test of this simplified model, since the results were *negative* (in the sense that the difference between theory and experiment is larger than the experimental error). If the result had been positive; i.e., if one or more sets of "reasonable" values of the unknown parameters furnished agreement with experiment, then the simplified model would be acceptable as an adequate one as long as the number of experimental points explained were larger than the number of adjustable parameters. However, the model would be subject to the further test of direct experimental determination of those parameters.

Another criticism of the model is that even with the use of high-speed digital computers it takes too long to integrate Eqs. (2) for realistic mechanisms, which, in the case of water, involve from six to 10 reactive species. This is not really a criticism of the validity of the model, but rather of its practical usefulness in explaining experimental results, suggesting new experiments and forecasting their outcome. However, integration of Eqs. (2) on presently available digital computers takes, for $n=10$, about 5 to 10 hr for a situation describable by a single space coordinate (see Sec. 4), so that several values of the initial distribution parameters could be tested if the other parameters were known. In addition, computers are already being constructed which are about 100 times faster than the common high-speed ones now in operation (one such computer is being constructed at the University of Illinois). These faster computers would permit rapid integration of Eqs. (2) for $n=10$ or more, thus decreasing the practical problem presented by the computational time. Also, simplified kinetic mechanisms can be used to describe the important features of the model without introducing serious errors[2b,26] (see Sec. 5).

Still another criticism of the model is connected with the explanation of the experimental absolute G values. Let us consider once more the case of aqueous solutions. For Co^{60} γ rays the yield of observable water decomposition, G_{-H_2O}, is about 4.6, whereas for Po^{210} α particles it is about 4.0.[40] However, in the vacuum uv

[40] See, for example, M. Lefort, Ann. Rev. Phys. Chem. **9**, 136 (1958).

photochemistry of these solutions, this G value is about 7.5 (the observed quantum yield for available radical pairs at 1900 A being about $\frac{1}{2}$).[18] This suggests that part of the absorbed energy in the radiolysis of aqueous solutions is being diverted from chemical action.[41] The G values for total water decomposition (including the chemically unobservable decomposition which is followed by regeneration of water) can be estimated by assuming that the G value for reformation of water is the sum of the G values for formation of H_2 and H_2O_2.[42] This estimate furnishes 5.8 for Co^{60} γ rays and 7.3 for Po^{210} α particles.[40] It would thus seem that there exists a track effect in these total G's. The question arises as to whether or not there is an intrinsic inconsistency between the diffusion-kinetic model of track effects and these observations. The answer to this question is negative. Indeed, if to explain the low G values for the radiolytic decomposition of aqueous solutions (as compared to the photolytic ones) it is necessary to assume a mechanism of energy dissipation which does not result in chemical change, this mechanism could show track effects and explain the difference between the total G's for Co^{60} γ rays and Po^{210} α particles. According to such an assumption, the energy required to form a radical pair by radiations of low and high LET would be different. There is no inconsistency between this and the diffusion-kinetic model. An alternate explanation is that correlation effects may be important for radiations of low LET, because there may be appreciable numbers of isolated spurs each consisting of a single H and OH pair.[6] For radiations of high LET the importance of this correlation may be greatly decreased owing to the high radical densities along the tracks.[43] Since our model permits the introduction of a certain amount of correlation, it is not inconsistent with this alternate explanation.

In conclusion, it seems that most of the criticisms of the diffusion-kinetic model, except the ones presented in the first paragraph of this section, are not very serious ones. However, the only test of the adequacy of the model can be the extent to which it can quantitatively explain experimental facts, guide in the choice of new experiments, and forecast their results. Insofar as water and dilute aqueous solutions are concerned, semiquantitative tests of the model have so far been quite satisfactory.[2b] The amount of factual information available at present is, however, insufficient to submit the model to a very strict test, but this information should be forthcoming in the near future.

4. METHOD FOR NUMERICAL INTEGRATION OF THE DIFFUSION-KINETIC EQUATIONS

4.1 Dimensionless Equations

For simplification of numerical integration procedures, it is convenient to introduce dimensionless variables. Let D^*, r^*, and c^* be three arbitrary constants having the dimensions of a diffusion coefficient, a length and a probability density, respectively. We introduce the dimensionless variables $\mathbf{r}'$, t', and c_i', defined by

$$\mathbf{r}'=\mathbf{r}/r^*,$$

$$t'=t/(r^{*2}/D^*),$$

and

$$c_i'(\mathbf{r}', t')=\frac{c_i[r^*\mathbf{r}, (r^{*2}/D^*)t']}{c^*}. \tag{18}$$

From Eqs. (18) and (2) there result the following differential equations for the dimensionless probability densities c_i' in terms of the dimensionless position coordinate $\mathbf{r}'$ and time coordinate t':

$$\frac{\partial c_i'(\mathbf{r}', t')}{\partial t'}=D_i'\nabla^2 c_i'-k_i'c_i'$$

$$-\sum_{j=1}^{n}k_{ij}'c_i'c_j'+\sum_{a=1}^{n}{}'k_{ai}'c_a'$$

$$+\sum_{b,d=1}^{n}(1-\tfrac{1}{2}\delta_{bd})k_{bi,di}'c_b'c_d'$$

$$i=1, 2, \cdots, n. \tag{19}$$

The quantities D_i', k_i' and k_{ij}' are dimensionless diffusion coefficients and rate constants defined respectively by

$$D_i'=D_i/D^*,$$

$$k_i'=k_i/(D^*/r^{*2}),$$

and

$$k_{ij}'=k_{ij}/(D/r^{*2}c^*). \tag{20}$$

The dimensionless quantities N', M', F' are defined by relationships similar to Eqs. (1) and (3) through (7) in which all quantities are primed. As a consequence of these definitions, the following relationship holds:

$$Q'(t')=\frac{Q[(r^{*2}/D^*)t']}{c^*r^{*3}}. \tag{21}$$

---

[41] In the photochemistry case the deviation of the quantum yield from unity might be due to a similar effect and/or to correlation, i.e., preferential recombination of H and OH originating from the same parent molecule.

[42] This assumption is justified by some recent calculations.[24,26,31] In these calculations, a two-radical one-scavenger diffusion-kinetic model was used. The initial distributions were spherical-Gaussian for low LET and infinite cylindrical-Gaussian for high LET. The rate constants were assumed time independent.

[43] H. A. Schwarz, J. M. Caffrey, Jr., and G. Scholes, J. Am. Chem. Soc. **81**, 1801 (1959).

Here Q represents any of the quantities N, M, or F. The primed counterpart of Eq. (9) is also valid.

4.2 Equations for Spherical and Longitudinally Homogeneous Cylindrical Symmetry

For the two extreme cases of low and high LET discussed in Sec. 2.5, a single space coordinate is sufficient to describe the problem; it is the distance r to the center of the spherically symmetrical spur or to the axis of the cylindrically symmetrical track. The Laplacian for both these cases, in terms of the dimensionless coordinates, is given by

$$\nabla^2=\frac{\partial^2}{\partial r'^2}+\frac{\alpha}{r'}\frac{\partial}{\partial r'};\quad \alpha=\begin{cases}2 \text{ for spherical symmetry}\\ 1 \text{ for cylindrical symmetry.}\end{cases} \tag{22}$$

Since, in an infinitely long cylindrical track, all species are present in infinite amount, it becomes convenient in this case to redefine the quantities N, M, F and their primed counterparts. Let us consider two planes perpendicular to the axis of the track and separated by an arbitrary distance L. We may consider the region between these planes to be our system and calculate the corresponding values of N, M, F. These will now be finite (except, of course, for species originally present in infinite amount). If we now divide these quantities by L, the results will be independent of L, owing to the homogeneity along directions parallel to the track axis. These new quantities are the ones which will be considered for this cylindrically symmetrical case, although the old symbols will be used to represent them. The values of N_i then represent the average linear number density of particles X_i along the axis of the track, corresponding reinterpretations being given to the several M's and F's. Under these conditions, the mathematical system (for the purpose of evaluation of space intergrals) is a two-dimensional plane perpendicular to the axis of the track. All relations involving N's, M's, and F's previously given continue to be valid for these redefined quantities.

4.3 Finite-Difference Approximation of Diffusion-Kinetic Equations

A finite difference approximation[44,45] of Eqs. (19) involving an explicit discretization method will now be introduced for the cases discussed in Sec. 4.2. The rate constants are assumed to be time-independent. Let $\Delta r'$ and $\Delta t'$ be small increments in the variables r' and t', respectively. Let $c_i'(m, k)$ represent c_i' at $r'=m\Delta r'$ and $t'=k\Delta t'$, m and k being nonnegative integers. Then, for sufficiently small values of the two increments, the following expressions hold:

$$\left(\frac{\partial^2 c_i'}{\partial r'^2}\right)_{m\Delta r',k\Delta t'}=\frac{c_i'(m+1,k)-2c_i'(m,k)+c_i'(m-1,k)}{(\Delta r')^2}, \tag{23}$$

$$\left(\frac{\partial c_i'}{\partial r'}\right)_{m\Delta r',k\Delta t'}=\frac{c_i'(m+1,k)-c_i'(m-1,k)}{2\Delta r'}, \tag{24}$$

$$\left(\frac{\partial c_i'}{\partial t'}\right)_{m\Delta r',k\Delta t'}=\frac{c_i'(m,k+1)-c_i'(m,k)}{\Delta t'}. \tag{25}$$

Substitution of Eqs. (22) through (25) into Eqs. (19) furnishes, for $m>0$

$$\begin{aligned}c_i'(m,k+1)=&\gamma D_i'[(1+\alpha/2m)c_i'(m+1,k)\\&+(1-\alpha/2m)c_i'(m-1,k)]\\&+(1-2\gamma D_i)c_i'(m,k)-\Delta t' c_i'(m,k)\\&\times\Big[k_i'+\sum_{j=1}^{n}k_{ij}'c_j'(m,k)\Big]+\Delta t'\sum_{a=1}^{n}{}'k_{a_i}'c_a'(m,k)\\&+\Delta t'\sum_{b,d=1}^{n}{}'(1-\tfrac{1}{2}\delta_{bd})k_{b_id_i}'c_b'(m,k)c_d'(m,k),\end{aligned} \tag{26}$$

where

$$\gamma=\Delta t'/(\Delta r')^2. \tag{27}$$

Equations (26) furnish $c_i'(m, k+1)$ as a function of $c_j'(m-1, k)$, $c_j'(m, k)$, and $c_j'(m+1, k)$, except for $m=0$. Since, for reasons of smoothness of the initial probability densities,

$$(\partial c_i'/\partial r')_{r'=0}=0, \tag{28}$$

Eqs. (19) present an indeterminacy at $r'=0$, which can be lifted by an application of l'Hospital's rule. This gives

$$\lim_{r'\to 0}[(1/r')(\partial c_i'/\partial r')]=(\partial^2 c_i'/\partial r'^2)_{r=0}. \tag{29}$$

From this expression and the finite difference approximation one gets

$$\begin{aligned}c_i'(0,k+1)=&2\gamma D_i'(1+\alpha)c_i'(1,k)\\&+[1-2(1+\alpha)\gamma D_i'c_i'(0,k)]\\&-\Delta t' c_i'(0,k)[k_i'+\sum_{j=1}^{n}k_{ij}'c_j'(0,k)]\\&+\Delta t'\sum_{a=1}^{n}{}'k_{a_i}'c_a'(0,k)\\&+\Delta t'\sum_{b,d=1}^{n}{}'(1-\tfrac{1}{2}\delta_{bd})k_{b_id_i}'c_b'(0,k)c_d'(0,k).\end{aligned} \tag{30}$$

[44] R. Courant, K. O. Friedrichs, and H. Levy, Math. Ann. **100**, 32 (1928).
[45] J. Todd, Communs. Pure Appl. Math. **9**, 597 (1956).

Equations (26) and (30) permit all c_i' at instant $t'=(k+1)\Delta t'$ to be calculated from a knowledge of all c_i' at the previous instant $t'=k\Delta t'$. Since all c_i' at time $t'=0$ are assumed to be known, these iterative relations permit the calculation of all c_i' for any m and k. A knowledge of these c_i' permits the calculation of all quantities N', M', and F' previously defined; any numerical integration method, such as Simpson's rule, can be used. For example,

$$N_i'(k\Delta t')=\tfrac{4}{3}\pi\alpha(\Delta r')^{\alpha+1}\sum_{m=1}^{\mathbf{m}}(2,1)m^{\alpha}c_i'(m,k), \quad (31)$$

where $(2, 1)$ is by definition 2 for odd values of m and 1 for even values, and $\mathbf{m}$ is a sufficiently large integer so that increasing it changes N_i' by a negligible amount. It should be remembered that for species X_i present in a finite amount, $m^{\alpha+1}c_i'(m, k)\to 0$ as $m\to\infty$.

4.4 Stability and Convergence of Finite Difference Approximation

Equations (2) form a system of quasi-linear parabolic equations of the type

$$\partial u(r,t)/\partial t=D(r,t)(\partial^2 u/\partial r^2)+a(r,t)(\partial u/\partial r)+b(r,t,u). \quad (32)$$

John[46] proved that the stability and convergence conditions of the finite difference equations associated with Eq. (32) are similar to those which apply to the linear parabolic equation

$$\partial u(r,t)/\partial t=D(r,t)(\partial^2 u/\partial r^2)+a(r,t)(\partial u/\partial r)+b(r,t). \quad (33)$$

Although these results are not rigorously applicable to Eqs. (2), an investigation of the stability conditions which hold for related linear equations seems to be the best available guide to the stability criteria for nonlinear cases. Let us then consider the linear equations obtained from Eqs. (19) by setting all rate constants equal to zero. (Although the first-order disappearance term is linear, its inclusion can be shown[45] not to affect the stability conditions for equations of this type.) The corresponding finite difference equations are obtained from Eqs. (30) and (27) by making this same substitution. They become, respectively,

$$c_i'(0,k+1)=[1-2(1+\alpha)\gamma D_i']c_i'(0,k)+2\gamma D_i'(1+\alpha)c_i'(1,k) \quad (34)$$

$$c_i'(m,k+1)=\gamma D_i'(1-\alpha/2m)c_i'(m-1,k)+(1-2\gamma D_i)c_i'(m,k)+\gamma D_i'(1+\alpha/2m)c_i'(m+1,k). \quad (35)$$

Let $\mathbf{x}_{i,k}$ be the vector

$$\mathbf{x}_{i,k}=[c_i'(0,k), c_i'(1,k), c_i'(2,k)\cdots]. \quad (36)$$

Then Eqs. (34) and (35) can be written in the matrix form

$$\mathbf{x}_{i,k+1}=\mathbf{B}_i\mathbf{x}_{i,k}, \quad (37)$$

where the element $[B_i]_{mj}$ (mth row, jth column) of the matrix $\mathbf{B}_i$ is the coefficient of $c_i'(j,k)$ in the equation giving $c_i'(m, k+1)$. A necessary and sufficient condition for the stability, and hence for the convergence, of Eqs. (34) and (35), is that all eigenvalues λ of $\mathbf{B}_i$ satisfy the relationship $|\lambda|\leq 1+O(\Delta t')$, where

$$\lim_{\Delta t'\to 0}[O(\Delta t')/\Delta t']=A\neq 0,$$

A being finite. Bounds on the eigenvalues may be obtained from Gerschgorin's theorem,[47] a well-known theorem from matrix theory. The bounds thus obtained are

$$1-4(1+\alpha)\gamma D_i'\leq\lambda\leq 1,$$

which yield the stability criterion

$$\gamma D_i'\leq 1/[2(1+\alpha)]. \quad (38)$$

This is a sufficient condition, but it is readily apparent that a somewhat less stringent criterion is necessary for the spherical case. To see this, one notes that when $\alpha=2$, the element in the second row and first column of $\mathbf{B}_i$ vanishes, so that one of the eigenvalues of $\mathbf{B}_i$ is $1-6\gamma D_i'$. The remainder of the eigenvalues of $\mathbf{B}_i$ satisfy $(1-4\gamma D_i')\leq\lambda\leq 1$; hence for the spherical case a necessary and sufficient condition for stability is

$$\gamma D_i'\leq\tfrac{1}{3}. \quad (38')$$

Equations (38) and (38′) impose a restriction on the values of $\gamma=\Delta t'/(\Delta r')^2$, which can be used in Eqs. (34) and (35). Since, as stated above, stability and convergence conditions of the difference equations are similar, an analogous restriction of γ probably holds for Eqs. (26) and (30). In actual computations, the dividing line between stable and unstable behavior for the spherical case was found to be at approximately $\gamma D_i'=\frac{1}{3}$, just as Eq. (38′) would indicate. A value of $\gamma D_i'=0.2$, well within the limit indicated by Eq. (38), was consistently used for the cylindrical case.

4.5 Accuracy of Method and Computation Time

A program was prepared for Illiac for the integration of Eqs. (19) in the cases represented by Eq. (22), using the finite difference approximation of Eqs. (26) and (30) and Simpson's rule for the computation of the several space and time integrals. The program permits *any initial condition* to be considered. It also permits *any reaction mechanism* which belongs to the general type described in Sec. 2.3 to be considered. Provisions were made to permit an automatic increase in the value of $\Delta t'$ and $\Delta r'$ several times during a computation so as to decrease the computation time without affecting the

[46] F. John, Communs. Pure Appl. Math. **5**, 155 (1952).

[47] See for example, A. B. Farnell, SIAM Rev. **2**, 36 (1960).

accuracy. The maximum number of equations the program can handle is 10. For the accuracy described below, the average computational time per equation is 1 hr for equations corresponding to primary or secondary species and about 15 min for equations corresponding to solutes initially present. This information is given because the speed of Illiac is typical of many high-speed digital computers available at present (about 500 μsec per multiplication).

The accuracy of the numerical method was checked by two independent means. Since the linear and quasi-linear equations are subject to similar stability and convergence conditions,[46] the accuracy for these two kinds of equations should be about the same under similar conditions. For an initial condition which is Gaussian, an explicit analytic expression for the solution of

$$\partial c'(r', t')/\partial t' = D'[(\partial^2 c'/\partial r'^2) + (\alpha/r')(\partial c'/\partial r')] - k'c' \tag{39}$$

is known; the errors in the numerical solution can be directly determined for this case. Several representative values of the parameters were tried, and in all cases the values of the quantities N' and M' checked with the correct ones to within 1% or better for the computation times mentioned in the previous paragraph. Higher accuracies were obtained for finer meshes and hence larger computation times. A second accuracy check is provided by the primed counterparts of Eqs. (9). This conservation relation was satisfied to about the same accuracy of 1%. This tends to indicate that these two criteria are approximately equivalent. For nonlinear equations analytical solutions are not available, but the conservation relations should still be satisfied. These relations include, in addition to the primed counterparts of Eqs. (9), the ones involving the conservation of the number of atoms mentioned at the end of Sec. 2.7. They provide accuracy checks for the general case. It was found that for the same values of the mesh parameters (i.e., same $\Delta t'$ and $\Delta r'$), the accuracy in the computation as determined from the conservation relations was the same for linear and nonlinear equations. In the more than 200 cases run thus far, the conservation relations were obeyed to 1% or better.

The program described in this section assumes that the rate constants are time independent. A modification of this program which will permit the rate constants to be time dependent is now in preparation. This modification will permit consideration of correlation effects, as discussed in Sec. 3.

4.6 Equations for Cylindrical Symmetry with Variations in the Longitudinal Direction

As mentioned in Sec. 2.5, for radiations of intermediate LET's in which the spurs are not sufficiently close at the beginning of the chemical stage to form a homogeneous track, and not sufficiently far apart for no interaction to occur, two space dimensions are necessary to describe the problem. Let O_{xyz} be a system of Cartesian coordinates whose z axis coincides with the axis of the track. The two space coordinates can be taken as z and $\rho=(x^2+y^2)^{\frac{1}{2}}$, the latter being the distance of point $P(x, y, z)$ to the axis of the track. The corresponding dimensionless coordinates are

$$z'=z/r^*, \qquad \rho'=\rho/r^*, \tag{40}$$

in terms of which the Laplacian to be used in Eqs. (19) is

$$\nabla^2=(\partial/\partial\rho'^2)+(\partial^2/\partial z'^2)+(1/\rho')(\partial/\partial\rho'). \tag{41}$$

A program for the numerical integration of these equations is in preparation, using a method similar to that described in Sec. 4.4.

5. SIMPLIFIED MECHANISMS

Owing to the large number of presently unknown parameters which appear in the model, it is profitable to initially apply the program described in Sec. 4.4 to simplified kinetic mechanisms which require the use of fewer parameters but which still present some important features of the model. Below are several much simplified mechanisms and their corresponding diffusion-kinetic equations.

A. One-radical one-solute model:

$$\begin{aligned} &\mathrm{R}+\mathrm{R}\rightarrow\mathrm{R}_2 \qquad k_{\mathrm{RR}},\\ &\mathrm{R}+\mathrm{S}\rightarrow\mathrm{RS} \qquad k_{\mathrm{RS}},\\ &\partial c_{\mathrm{R}}/\partial t = D_{\mathrm{R}}\nabla^2 c_{\mathrm{R}} - k_{\mathrm{RR}}c_{\mathrm{R}}^2 - k_{\mathrm{RS}}c_{\mathrm{R}}c_{\mathrm{S}},\\ &\partial c_{\mathrm{S}}/\partial t = D_{\mathrm{S}}\nabla^2 c_{\mathrm{S}} - k_{\mathrm{RS}}c_{\mathrm{R}}c_{\mathrm{S}}. \end{aligned} \tag{42}$$

This model permits investigation of the effects of scavenger concentration and diffusion.

B. One-radical one-reactive-intermediate one-solute model:

$$\begin{aligned} &\mathrm{R}+\mathrm{R}\rightarrow\mathrm{R}_2 \qquad k_{\mathrm{RR}},\\ &\mathrm{R}+\mathrm{R}_2\rightarrow\mathrm{R}_3 \qquad k_{\mathrm{RR}_2},\\ &\mathrm{R}+\mathrm{S}\rightarrow\mathrm{RS} \qquad k_{\mathrm{RS}},\\ &\mathrm{R}_2+\mathrm{S}\rightarrow\mathrm{R}_2\mathrm{S} \qquad k_{\mathrm{R}_2\mathrm{S}},\\ &\partial c_{\mathrm{R}}/\partial t = D_{\mathrm{R}}\nabla^2 c_{\mathrm{R}} - k_{\mathrm{RR}}c_{\mathrm{R}}^2 - k_{\mathrm{RR}_2}c_{\mathrm{R}}c_{\mathrm{R}_2} - k_{\mathrm{RS}}c_{\mathrm{R}}c_{\mathrm{S}},\\ &\partial c_{\mathrm{R}_2}/\partial t = D_{\mathrm{R}_2}\nabla^2 c_{\mathrm{R}_2} - k_{\mathrm{RR}_2}c_{\mathrm{R}}c_{\mathrm{R}_2} - k_{\mathrm{R}_2\mathrm{S}}c_{\mathrm{R}_2}c_{\mathrm{S}} + \tfrac{1}{2}k_{\mathrm{RR}}c_{\mathrm{R}}^2,\\ &\partial c_{\mathrm{S}}/\partial t = D_{\mathrm{S}}\nabla^2 c_{\mathrm{S}} - k_{\mathrm{RS}}c_{\mathrm{R}}c_{\mathrm{S}} - k_{\mathrm{R}_2\mathrm{S}}c_{\mathrm{R}_2}c_{\mathrm{S}}. \end{aligned} \tag{43}$$

This model permits investigation of the effects of some secondary track reactions.

C. Two-radical two-solute model:

$$\begin{aligned} R+R &\rightarrow R_2 & k_{RR},\\ R+R^* &\rightarrow RR^* & k_{RR^*},\\ R^*+R^* &\rightarrow R_2^* & k_{R^*R^*},\\ R+S &\rightarrow RS & k_{RS},\\ R^*+S^* &\rightarrow R^*S^* & k_{R^*S^*}, \end{aligned} \tag{44}$$

$$\partial c_R/\partial t = D_R\nabla^2 c_R - k_{RR}c_R^2 - k_{RR^*}c_R c_{R^*} - k_{RS}c_R c_S,$$

$$\partial c_{R^*}/\partial t = D_{R^*}\nabla^2 c_{R^*} - k_{RR^*}c_R c_{R^*} - k_{R^*R^*}c_{R^*}^2 - k_{R^*S^*}c_{R^*}c_{S^*},$$

$$\partial c_S/\partial t = D_S\nabla^2 c_S - k_{RS}c_R c_S,$$

$$\partial c_{S^*}/\partial t = D_{S^*}\nabla^2 c_{S^*} - k_{R^*S^*}c_{R^*}c_{S^*}.$$

D. Two-radical one-reactive intermediate one-solute model:

$$\begin{aligned} R+R &\rightarrow R_2 & k_{RR},\\ R+R^* &\rightarrow RR^* & k_{RR^*},\\ R^*+R^* &\rightarrow R_2^* & k_{R^*R^*},\\ R+R_2^* &\rightarrow RR_2^* & k_{RR_2^*},\\ R+S &\rightarrow RS & k_{RS},\\ R^*+S &\rightarrow R^*S & k_{R^*S},\\ R_2^*+S &\rightarrow R_2^*S & k_{R_2^*S}, \end{aligned}$$

$$\partial c_R/\partial t = D_R\nabla^2 c_R - k_{RR}c_R^2 - k_{RR^*}c_R c_{R^*} - k_{RR_2^*}c_R c_{R_2^*} - k_{RS}c_R c_S,$$

$$\partial c_{R^*}/\partial t = D_{R^*}\nabla^2 c_{R^*} - k_{RR^*}c_R c_{R^*} - k_{R^*R^*}c_{R^*}^2 - k_{R^*S}c_{R^*}c_S,$$

$$\partial c_{R_2^*}/\partial t = D_{R_2^*}\nabla^2 c_{R_2^*} - k_{RR_2^*}c_R c_{R_2^*} - k_{R_2^*S}c_{R_2^*S} + \tfrac{1}{2}k_{R^*R^*}c_{R^*}^2,$$

$$\partial c_S/\partial t = D_S\nabla^2 c_S - k_{RS}c_R c_S - k_{R^*S}c_{R^*}c_S - k_{R_2^*S}c_{R_2^*}c_S. \tag{52}$$

This model permits investigation of the effects of secondary reactions between one kind of radical and a secondary product of the other kind of radical.

In each of these models the importance of the initial conditions should be carefully investigated. For example, non-Gaussian distributions, including bimodal ones, should be considered.

Future papers in this series will describe the results of investigating models of this kind.